

Director

Department of Pesticide Regulation

Gray Davis Governor Winston H. Hickox Secretary, California Environmental Protection Agency

MEMORANDUM

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SUBJECT: PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND ACUTE

TOXICITY TESTING OF MONTHLY SURFACE WATER MONITORING FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY,

JULY 2000 (STUDY 183)

SUMMARY

During July 2000, surface water samples were collected from five sites in Orange County, California. At one site a filter strip was added to the waterway as part of a mitigation study so samples were collected at the inflow and outflow of the filter strip. At the time of sampling, the filter strip had not yet been planted, only the basin was constructed. Concentrations of bifenthrin and diazinon were similar at the inflow and outflow. Samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos. There were three detections of bifenthrin with concentrations ranging from 0.23 1 to 0.273 parts per billion (ppb) at the three nursery sites. Diazinon and malathion were detected at five and one site, respectively. Toxicity was tested at the San Diego Creek, an integrated site. This site had significant mortality (30%) to *Ceriodaphnia dubia* in the water collected. The toxicity at the Creek could be attributed to diazinon and other unknown toxicants.

SCOPE OF THIS MEMORANDUM

This memorandum reports results of water sampling conducted by the Department of Pesticide Regulation (DPR), under interagency agreement with the California Department of Food and Agriculture (CDFA), for the Red Imported Fire Ant (RIFA) control project, Data included here are from the July 12 and 13, 2000 monitoring, and encompass results from both chemical analyses and aquatic biotoxicity testing. This memorandum summarizes results for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and eight organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methyl parathion, and



phosmet. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos are used in the RIFA control program. The other seven organophosphates are in our multiresidue analytical method and are included in this report to assist in the interpretation of the toxicity results. Acute toxicity results using *Ceriodaphnia dubia* are also included. An in-depth interpretation of data is not included here, but will be provided in the final report when the 2000 pesticide use report becomes available.

Reports of the monthly surface water sampling events will continue through the conclusion of the study. This memo is the eleventh in the monthly sampling series. You can request previous sampling results memos by calling the number above or you may view or download them from DPR's website at <www.cdpr.ca.gov/docs/rifa>.

MATERIALS AND METHODS

Sample and Data Collection

On July 12 and 13, 2000, surface water samples were collected at five creeks within the Orange County treatment area (Table 1 and Figure 1). Sites A, B, I, and J were not sampled due to chemistry laboratory overload. Site H was not sampled because of insufficient water. Site G was sampled at two different points on the waterway. A 160-yard filter strip was added to the waterway as part of a mitigation study at a commercial nursery so samples were collected at the inflow (site G1) and outflow (site G2) of the filter strip. At the time of this sampling, the filter strip had not yet been planted Toxicity samples were only collected at site E. This sampling event did not coincide with measurable rainfall.

Table 1. Sampling site descriptions in Orange County, California

Tuole 1. Sampling site descriptions in Grange County, Camonia								
Site #	Description	Coordinates						
A	Bolsa Chica Channel at Westminster Ave.	N 33°45'35", W 118'02'36"						
В	East Garden Grove Channel at Gothard St.	N 33°43'03", W 117°59'59"						
C	Westcliff Park	N 33°37'24", W 117°54'02"						
D	Bonita Creek at San Diego Creek	N 33°39'03", W 117'51'49"						
E	San Diego Creek at Campus Dr.	N 33°39'18", W 117°50'44"						
F	Hines at Weir	N 33°42'30", W 117'44'19"						
G	El Modeno	N 33°42'43", W 117'44'16"						
Н	Marshburn Slough at Irvine Blvd.	N 33°41'45", W 117'44'02"						
I	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117'40'43"						
J	Arrovo Trabuco at Oso Parkwav	N 33°35'06", W 117°38'09"						

John Sanders October 5, 2000 Page 3

All water samples were collected at center channel using a 1 O-liter stainless steel bucket and divided into one-liter amber sample bottles using a Geotech® 1 O-port splitter. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5. Because diazinon rapidly degrades under acidic conditions, it was analyzed from a separate, un-acidified sample. Samples designated for toxicity testing were delivered to the testing laboratory within 36 hours of collection. All samples were stored on wet ice or in a 4" C refrigerator until transported to the appropriate laboratory for analysis.

Toxicity Tests

Acute toxicity testing was conducted by the Department of Fish and Game (DFG) Aquatic Toxicity Laboratory following current U.S. Environmental Protection Agency (US. EPA) procedures using a cladoceran, *Ceriodaphnia dubia*, (U.S. EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water. Data were reported as percent mortality.

Environmental Measurements

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using an IQ Scientific Instruments@ (model IQ 150) pH meter. EC, water temperature, and DO were measured using an YSI® multi parameter meter (model 85). Additionally, the DFG Aquatic Toxicity Laboratory measured alkalinity, hardness, and ammonia on the samples to be tested for toxicity. Totals of alkalinity and hardness were measured with a Hach7 titration kit, Ammonia was determined using an Orion® 95-12 ammonia selective electrode attached to an Orion® specific ion meter (model 290A).

Insecticide Analyses

All water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, fonofos, malathion, methidathion, methyl parathion, and phosmet. The CDFA Center for Analytical Chemistry performed all analysis using gas chromatography and a flame photometric detector for the eight organophosphorus insecticides; a high performance liquid chromatography and a ultra violet detector for fenoxycarb, hydramethylnon, and pyriproxyfen; and gas chromatography with an electron capture detector confirmed with a mass selective detector for bifenthrin. The reporting limit (reliable detection levels) for chlorpyrifos and diazinon is 0.04 ppb, 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

John Sanders October 5, 2000 Page 4

RESULTS and DISCUSSIONS

Insecticide Concentrations

A total of six samples were analyzed for the eight organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits (Table 2). Diazinon was detected in five samples and ranged from 0.102 to 0.332 ppb. Malathion was detected in one sample with a concentration of 0.124 ppb. Bifenthrin was detected in three samples with concentrations ranging from 0.23 1 to 0.273 ppb. There were no detections of fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, dimethoate, fonofos, methidathion, methyl parathion, or phosmet. Sites G1 and G2 both had detections of bifenthrin and diazinon. The bifenthrin detection recorded at site F and the bifenthrin and diazinon detections at site G were both collected at commercial nurseries. Samples collected at integrated site E, in a creek downstream from sites F and G, showed a detection of diazinon. Sites C and D, which mainly drain urban areas, both had detections of diazinon; site C had an additional detection of malathion. Of the twelve insecticides tested, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with U.S. Department of Agriculture quarantine requirements. All of the organophosphorus insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses or parks for the control of other insect pests. Malathion, diazinon, and chlorpyrifos are widely available for homeowner use.

Table 2. Insecticide concentrations and acute toxicity in surface water samples, July 12 and 13, 2000, Orange County, California.

Concentration in pbb									% Acute ortality'				
Site	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	fonofos	malathion	methidathion	m. parathion	phosmet	C. dubia
A	NS ⁴	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
В	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
C	ND^2	ND	ND	ND	ND	0.272	ND	ND	0.124	ND	ND	ND	NS
D	ND	ND	ND	ND	ND	0.332	ND	ND	ND	ND	ND	ND	NS
E	ND	ND	ND	ND	ND	0.089	ND	ND	ND	ND	ND	ND	$30/0^3$
F	0.273	ND	ND	NE) NE	ND	ND	ND	ND	ND	ND	ND	NS
G1	0.231	ND	NE) NI) NE	0.11	ND	ND	ND	ND	ND	ND	NS
G2	0.273	ND	ND	ND	ND	0.102	ND	ND	ND	ND	ND	ND	NS
Н	NW ⁵	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NW	NS
I	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
J	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

¹ Two numbers are reported for each toxicity test. The first number is the result from the sample; the second from the corresponding control.

Toxicity Data

Toxicity samples were taken from one integrated site within the treatment area. Sample from site E was acutely toxic to C. dubia causing 30 % mortality (Table 2). Site E drains an integrated site and had a detection of diazinon below the LC_{50} for C. dubia (Table 3). The toxicity at site E could be attributed to diazinon and other unknown toxicants.

 $^{^{2}}$ ND = none detected at the reporting limit for that chemical.

³ The difference in mortality between the sample and the corresponding control are significant using Wilcoxon two-sample test.

 $^{^4}$ NS = not sampled

⁵ NW= no water discharged

Table 3. LC₅₀'s of insecticides (ppb) for three aquatic species and U.S. EPA fresh water quality criteria.

-				Fresh Water Quality Criteria
Pesticide	Rainbow trout'	D . $magna^1$	C. dubia	(Acute)
Bifenthrin	0.15	0.16	NA ²	NA
Chlorpyrifos	3	1.7	0.13^{3}	0.083^4
Diazinon	2600	0.96	0.51^{5}	0.090^{6}
Dimethoate	6200	4700	NA	NA
Fenoxycarb	1600	400	NA	NA
Fonofos	50	1	NA	NA
Hydramethylnon	160	1140	NA	NA
Malathion	170	1.8	$1.14^7 - 2.12^8$	NA
Methidathion	10	3	2.2^{9}	NA
Methyl parathion	2700	7.3	NA	NA
Phosmet	230	8.5	NA	NA
Pyriproxyfen	>325 ¹⁰	400^{11}	NA	NA NA

Data from Tomlin, C.D.S., 1997

Environmental Measurements

Table 4 presents the data for DO, temperature, pH, and EC. Ammonia, alkalinity, and hardness are reported for site E only since these measurements are taken with the toxicity tests. Water temperature ranged from 18.5 to 26.0" C; DO ranged from 6.46 to 11.66 mg/L; pH ranged between 8.2 to 8.7; EC ranged from 490 to 3298 μS/cm; ammonia was 3.68 mg/L NH₃; alkalinity was 180 mg/L CaCO₃; and hardness was 742 mg/L CaCO₃. The California Regional Water Quality Control Board, Water Quality Control Plan, Santa Ana River Basin (1995), and the Water Quality Control Plan, San Diego Basin (1994), list the following water quality guidelines as acceptable: DO above 5.0 mg/L, pH between 6.5 and 8.5, and water temperature no higher than 78°F (25.5°C). The Santa Ana River Basin plan determines ammonia levels to be dependent upon water temperature and pH, while the San Diego Basin plan states that ammonia

² NA= Not Available

³ Data from Menconi and Paul, 1994

⁴ Data from U.S. EPA, 1994

⁵ Data from Menconi and Cox, 1994

⁶ Proposed U.S. EPA data

⁷ Data from Nelson and Roline, 1998.

⁸ Data from Ankley et al., 1991

⁹Data from Menconi and Siepmann, 1994

¹⁰ Data from Bowman, Jane H., 1989

¹¹ Data from Burgess, David, 1989

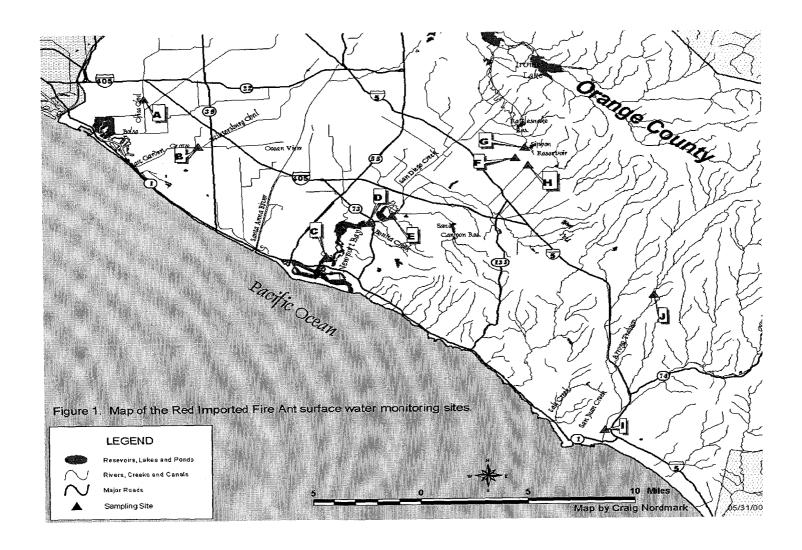
levels shall not exceed $0.025\ mg/L$. The plans do not provide an acceptable range for EC, alkalinity, or hardness. The pH at sites C, E, G1 and G2 were above the maximum guideline as were the water temperatures at sites G1 and G2.

Table 4. Water quality measurements at sampling sites, July 2000, Orange County, California.

Site	Temperature	pН	Dissolved	Electroconductivity	Ammonia	Alkalinity	Hardness
	(°C)		Oxygen (mg/L)	(µS/cm)	mg/L	mg/L CaCO ₃	mg/L CaCO ₃
A	NS	NS	NS	NS	NS	NS	NS
В	NS	NS	NS	NS	NS	NS	NS
C	20.7	8.7	10.28	490	NR	NR	NR
D	18.5	8.3	6.46	3150	NR	NR	NR
E	24.0	8.6	11.66	3253	3.68	180	742
F	21.4	8.2	8.45	3298	NR	NR	NR
G1	25.9	8.6	NT	1850	NR	NR	NR
G2	26.0	8.6	8.22	1489	NR	NR	NR
Н	NW	NW	NW	NW	NS	NS	NS
I	NS	NS	NS	NS	NS	NS	NS
J	NS	NS	NS	NS	NS	NS	NS

NT= Not taken; NS= Not sampled

NW= No water discharged; NR= No reading available



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John Sanders October 5, 2000 Page 10

Precipitation data obtained from The University of California Statewide Integrated Pest Management Project, California Weather Databases. www.ipm.ucdavis.edu/WEATHER/